

FUEL ADDITIVES FOR FUEL CELL

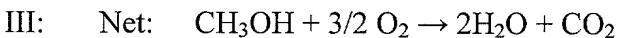
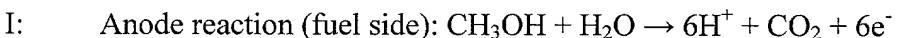
1 Technical Field

2 The technical field generally relates to fuel cells and in particular to fuel additives
3 that enhance performance of liquid-type fuel cells.

4 Background

5 A fuel cell is an electrochemical apparatus wherein chemical energy generated
6 from a combination of a fuel with an oxidant is converted to electric energy in the
7 presence of a catalyst. The fuel is fed to an anode, which has a negative polarity, and the
8 oxidant is fed to a cathode, which, conversely, has a positive polarity. The two electrodes
9 are connected within the fuel cell by an electrolyte to transmit protons from the anode to
10 the cathode. The electrolyte can be an acidic or an alkaline solution, or a solid polymer
11 ion-exchange membrane characterized by a high ionic conductivity. The solid polymer
12 electrolyte is often referred to as a proton exchange membrane (PEM).

13 In fuel cells employing liquid fuel, such as methanol, and an oxygen-containing
14 oxidant, such as air or pure oxygen, the methanol is oxidized at an anode catalyst layer to
15 produce protons and carbon dioxide. The protons migrate through the PEM from the
16 anode to the cathode. At a cathode catalyst layer, oxygen reacts with the protons to form
17 water. The anode and cathode reactions in this type of direct methanol fuel cell are
18 shown in the following equations:



22 The goal in methanol fuel processing is complete methanol oxidation for
23 maximum energy generation shown in the equation. Catalysts that promote the rates of
24 electrochemical reactions, such as oxygen reduction and hydrogen oxidation in a fuel cell
25 are often referred to as electrocatalysts. Electrocatalysts are important because the
26 energy efficiency of any fuel cell is determined, in part, by the overpotentials necessary at
27 the fuel cell's anode and cathode. In the absence of an electrocatalyst, a typical electrode
28 reaction occurs, if at all, only at very high overpotentials. Thus, the oxidation and
29 reduction reactions require catalysts in order to proceed at useful rates.

30 *Carbon monoxide (CO) poisoning of the catalyst*

31 Platinum (Pt), an expensive metal, is the best catalyst for many electrochemical
32 reactions, including methanol oxidation. A major obstacle in the development of

1 methanol fuel cells is the loss of electrochemical activity of even the best electrocatalyst
2 due to "poisoning" by CO. CO is an intermediate in the oxidation of methanol to carbon
3 dioxide (CO₂). CO is adsorbed at the surface of the Pt due to its special molecular
4 structure and thus blocks the access of new fuel molecules to the catalytically active Pt
5 centers.

6 CO is a severe poison to Pt electrocatalysts. It significantly reduces fuel cell
7 performance even at levels of 1-10 ppm. A fuel cell which would be useful for
8 commercial applications would preferably be tolerant of CO levels produced in a
9 relatively uncomplicated fuel system, i.e., 100 ppm or greater.

10 Substantial effort has been devoted to developing a multi-element catalyst such as
11 Pt-Ru and Pt-Ru-Os. The addition of Ruthenium (Ru), for example, helps convert CO
12 into CO₂ and relieves the Pt from being poisoned. Attempts have also been made to
13 further reduce the CO concentration, and particularly through a selective oxidation
14 process for the CO. Conventionally, the oxidation of CO to CO₂ occurs in the presence of
15 a catalyst and at temperatures above 150°C.

16 PEM fuel cells, which have potential application in mass transportation, are very
17 sensitive to CO poisoning. Conventional PEM membranes, such as NAFIONTM, must
18 contain significant amounts of water to conduct protons from the electrode reactions.
19 Accordingly, PEM fuel cells cannot operate at temperatures over about 100°C, and
20 preferably operate at temperatures around 80°C. At these operating temperatures, CO
21 strongly adsorbs to the Pt catalyst to poison the fuel cell performance.

22 Thus, there remains a need to reduce the level of CO in the fuel system to improve
23 liquid-type fuel cell performance in an effective and commercially viable manner.

24 *Wettability of the electrodes*

25 Adequate wetting of the electrodes is another major problem for liquid-type fuel
26 cells. To provide a large reaction area, the electrode structures in a liquid-type fuel cell
27 need to be very porous and the liquid fuel solution needs to wet all pores. In addition,
28 CO₂ that is evolved at the fuel side electrode needs to be effectively released from the
29 zone of reaction. Adequate wetting enhances the release of CO₂ from the electrode. In
30 PEM fuel cells, the PEM also requires water to be effective in conducting protons.

31 Conventional gas diffusion type fuel cell anode structures are not suitable for use
32 in liquid-type fuel cells. These conventional electrodes have poor fuel wetting properties.
33 The conventional electrodes, however, can be modified for use in liquid-type fuel cells by

1 coating them with an electrode additive that improve their wetting properties, such as
2 NAFION™ which also serves as a PEM.

3 US Pat. No. 6,248,460 describes a method of wetting an electrode within a liquid-
4 type fuel cell having a sulfuric acid electrolyte by employing perfluorooctanesulfonic acid
5 as an additive to the fuel mixture of the fuel cell. However, the invention is directed to a
6 very specific application, i.e., improving performance of fuel cells having a sulfuric acid
7 electrolyte, and is not applicable to other types of liquid-type fuel cells, such as fuel cells
8 having a PEM.

9 *“Futile oxidation” at the anode*

10 As shown in equation II, the cathode of liquid-type fuel cells is exposed to air
11 where the protons react with oxygen to produce water. Some oxygen will inevitably
12 dissolve in the fuel and will be carried to the anode side of the fuel cell. The oxygen will
13 then be oxidized into oxygen ions by the catalyst on the anode. The oxygen ions will then
14 react with the protons produced on the anode by equation I, and form water on the anode.
15 This “futile oxidation” prevents the transfer of protons from the anode to the cathode and
16 hence diminishes the current generated by the fuel cell reaction. There remains a need to
17 efficiently remove the dissolved oxygen from the fuel of a liquid type fuel cell.

18 *Impurities in the fuel*

19 Impurities in the fuel of a fuel cell may inhibit the desired electrochemical
20 reaction. For example: a methanol based liquid fuel may contain trace amount of sulphur
21 or metal ions, such as Fe^{++} , Cu^{++} , Cr^+ , Ni^+ , and Zn^{++} , that are detrimental to the electrolyte
22 and/or catalyst. The impurities may originate from the fuel supply itself or enter the fuel
23 from elsewhere in the system. Some of the impurities may be chemically adsorbed or
24 physically deposited on the surface of the anode catalyst, blocking the active catalyst sites
25 and preventing these portions of the anode catalyst from inducing the desired
26 electrochemical fuel oxidation reaction.

27 In the absence of countermeasures, the adsorption or deposition of catalyst
28 poisons may be cumulative, so even minute concentrations of poisons in a fuel stream,
29 may, over time, result in a degree of catalyst poisoning which is detrimental to fuel cell
30 performance.

31 Conventional methods for addressing the problem of fuel impurities include
32 physical filtration and/or chemical treatment of the fuel to remove the impurities. The
33 purification process can be tedious and expensive, and requires specially designed
34 equipment.

1 **Summary**

2 A method of enhancing performance of liquid-type fuel cells by adding additives
3 to the liquid fuel is disclosed. Different additives may be employed to perform different
4 functions, such as reducing CO poisoning of the catalyst, increasing wettability of the
5 electrodes, or removing dissolved oxygen and impurities in the fuel. The additives may
6 be used individually, or premixed in a desired ratio for a given type of fuel cell. The
7 additives may be used on a regular basis to improve fuel efficiency and prolong the life
8 span of fuel cells. The additives may also be pre-packed for field use when high quality
9 fuel is not available. These additives thus provide a convenient and cost-effective way of
10 improving performance of a liquid-type fuel cell.

11 In an embodiment, hemoglobin may be used as an additive to absorb CO in the
12 fuel and prevent CO poisoning of the catalyst in a fuel cell.

13 In another embodiment, a wettability control agent, such as a surfactant, may be
14 used as an additive to improve the wetting of the porous electrode.

15 In another embodiment, an oxygen scavenger, such as ascorbate, may be used as
16 an additive to remove oxygen dissolved in the fuel and prevent the futile oxidation on the
17 anode of the fuel cell.

18 In yet another embodiment, a chelating agent, such as EDTA, may be used as an
19 additive to remove metal ions from the fuel to prevent the poisoning of the electrode.

20 Additional advantages and novel features will be set forth in part in the
21 description which follows, and in part will become apparent to those skilled in the art
22 upon examination of the following or may be learned by practice of the invention.

23 **Detailed Description**

24 A variety of materials can be used as fuel additives for fuel cell applications.
25 Different materials may serve different functions. In an embodiment, hemoglobin may be
26 used as a fuel additive to prevent CO poisoning of Pt based catalyst.

27 Hemoglobin is the major component of red blood cells which transport oxygen
28 from the lungs to body tissues and facilitates the return transport of CO₂. Hemoglobin is
29 a 64,400 kD protein. Each hemoglobin molecule is a tetramer of four smaller polypeptide
30 subunits known as globins. A hemo group, which is an iron-protoporphyrin complex, is
31 associated with each polypeptide subunit, and is responsible for the reversible binding of
32 a single molecule of oxygen. Normal adult hemoglobin is made up of two different kinds
33 of polypeptide globins. A first globin, known as alpha globin, contains 141 amino acid
34 residues. The second, known as beta globin, contains 146 amino acid residues. In normal

1 adult hemoglobin, two of each kind of globin are arranged in the form of a truncated
2 tetrahedron which has the overall shape of an ellipsoid.

3 Ligands that bind hemoglobin include CO, NO, CN⁻, and the most physiologically
4 relevant ligand, oxygen. CO is well known to be highly toxic to the oxygen transport
5 function of hemoglobin. In humans, a small amount of CO will cause serious problems, a
6 blood CO concentration of 400 ppm will result in headache and discomfort, and 4000
7 ppm can be fatal in less than one hour. The reason for this toxicity is that hemoglobin is
8 235 times more reactive to CO than to oxygen. Binding of CO molecules to hemoglobin
9 decreases the total oxygen carrying capacity of blood by rendering a portion of the
10 hemoglobin molecule unusable for oxygen binding, it also shifts the conformation of the
11 remaining hemoglobin molecule such that the hemoglobin binds the oxygen more avidly,
12 thus making it more difficult for oxygen to be released to the tissues and therefore
13 starving the tissue and organs of vital oxygen supplies. In other words, CO binds to
14 hemoglobin in a way similar to its binding to Pt. Therefore, hemoglobin may be used as a
15 fuel additive to preferentially bind CO and relieve the Pt catalyst from being poisoned by
16 CO.

17 Hemoglobin is available in either powder or liquid form. The powder form can be
18 dissolved in water or water containing fuels. It is available from, for example, Sigma-
19 Aldrich Inc. The liquid form is available from Biopure as Oxyglobin® solution.

20 Generally, the amount of hemoglobin that may be added to the fuel is in the range
21 of 0.0001-1% by weight.

22 In another embodiment, the additive may be a surfactant that decreases interfacial
23 tension of the liquid/catalyst interface and leads to the uniform wetting of the electrode
24 pores and particles by the fuel and water solution, yielding enhanced utilization of the
25 electrocatalyst. Further, the improved wettability also facilitates the release of carbon
26 dioxide from the pores of the electrode.

27 The surfactant may be an anionic, cationic, amphoteric, nonionic surfactant, or a
28 mixture of compatible surfactants.

29 Examples of anionic surfactants are water-soluble soaps or water-soluble synthetic
30 surface active compounds. Examples of the soaps are unsubstituted or substituted
31 ammonium salts of higher fatty acids (C10 -C22), such as the sodium or potassium salts
32 of oleic acid or stearic acid or of natural fatty acid mixtures such as coconut oil or tallow
33 oil, alkali metal salts, alkaline earth metal salts or fatty acid methylaurin salts. Examples

1 of synthetic surfactants are alkylarylsulphonates, sulphonated benzimidazole derivatives,
2 fatty alcohol sulphates, or fatty alcohol sulphonates.

3 Examples of alkylarylsulphonates are the calcium, sodium or triethanolamine salts
4 of dodecylbenzenesulphonic acid, dibutylnaphthalenesulphonic acid, of a condensate of
5 naphthalenesulphonic acid and formaldehyde or the phosphate salt of the phosphoric acid
6 ester of an adduct of p-nonylphenol with 4 to 14 moles of ethylene oxide. Examples of
7 sulphonated benzimidazole derivatives are 2 sulphonic acid groups and one fatty acid
8 radical containing approximately 8 to 22 carbon atoms. Examples of fatty alcohol
9 sulphates or sulphonates are unsubstituted or substituted ammonium salts such as C8 -
10 C22 alkyl radical including the alkyl moiety of acyl radicals such as the calcium or
11 sodium salt of lignosulphonic acid, of a mixture of fatty alcohol sulphates from naturally
12 occurring fatty acids, of dodecylsulphate, alkali metal salts or alkaline earth metal salts or
13 the salts of sulphated and sulphonated fatty alcohol/ethylene oxide adducts.

14 Examples of non-ionic surfactants are polyglycol ether derivatives of aliphatic or
15 cycloaliphatic alcohols having approximately 3 to 30 glycol ether groups and
16 approximately 8 to 20 carbon atoms in the (aliphatic) hydrocarbon moiety; saturated or
17 unsaturated fatty acid and alkylphenols having approximately 6 to 18 carbon atoms in the
18 alkyl moiety of the alkylphenols; water-soluble adducts of polyethylene oxide with
19 ethylenediaminopolypropylene glycol, polypropylene glycol, or alkylpolypropylene
20 glycol having approximately 1 to 10 carbon atoms in the alkyl chain, having
21 approximately 20 to 250 ethylene glycol ether groups and approximately 10 to 100
22 propylene glycol ether groups in the usual ratio of 1 to 5 ethylene glycol
23 moiety:propylene glycol moiety; fatty acid esters of polyoxyethylene sorbitan such as
24 polyoxyethylene sorbitan trioleate; octylphenoxypropoxyethanol; polyethylene glycol;
25 tributylphenoxypropoxyethanol; polypropylene/polyethylene oxide adducts; castor oil
26 polyglycol ethers; nonylphenolpolyethoxyethanols.

27 Examples of cationic surfactants are quaternary ammonium salts in the form of
28 halides, methylsulphates or ethylsulphates which have as N-substituent at least one C8 -
29 C22 alkyl radical or unsubstituted or halogenated lower alkyl or benzyl or hydroxy-lower
30 alkyl radicals, such as stearyltrimethylammonium chloride or benzylid(2-
31 chloroethyl)ethylammonium bromide.

32 Examples of amphoteric surfactants are the aminocarboxylic and aminosulphonic
33 acids and salts thereof such as alkali metal 3-(dodecylamino)propionate and alkali metal

1 3-(dodecylamino)propane-1-sulphonate or alkyl and alkylamido betaines such as
2 cocamidopropyl betaine.

3 Examples of surfactants which may be used in the combination are surfactants from the
4 Teric.RTM. series such as N4 Teric, Teric BL8, Teric 16A16, Teric PE61, Alkanate
5 3SL3, N9 Teric, G9 A6 Teric or from the Rhodafac.RTM series such as Rhodafac RA
6 600. Further examples are Calgon.RTM (sodium hexametaphosphate), Borax.RTM
7 (sodium decahydrate borate), soap, sodium lauryl sulphate, or sodium cholate.

8 Generally, the amount of surfactant that may be added to the liquid fuel is in the
9 range of 0.0001-1% by weight.

10 In another embodiment, the fuel additive may be an oxygen scavenger that
11 absorbs oxygen in the fuel and therefore, reduces the futile oxidative reaction on the
12 anode. Examples of oxygen scavengers include, but are not limited to, sodium sulfite,
13 sodium bisulfite, ascorbate, hydrazine, hydroquinone, benzmay, and sulfhydryl
14 compounds.

15 Generally, the amount of oxygen scavenger that may be added to the liquid fuel is
16 in the range of 0.0001- 1% by weight.

17 In yet another embodiment, the fuel additive may be a chelating agent that
18 removes the metal ions that have a detrimental effect on the electrodes. Examples of
19 chelating agents include, but are not limited to, ethylenediaminetetraacetic acid (EDTA)
20 and trans-1,2-diaminocyclohexane-N,N,N',N'-tetraacetic acid (CDTA), and salts thereof.

21 Generally, the amount of chelating agent that may be added to the liquid fuel is in
22 the range of 0.0001- 1% by weight.

23 The additives may be added individually based on needs, or pre-mixed in a
24 desired ratio for a given type of fuel cell. The additives can be used on a regular basis to
25 improve fuel efficiency and prolong the life span of fuel cells. They can also be pre-
26 packed for field use when high quality fuel is not available. These additives thus provide
27 a convenient and cost-effective way of improving performance of liquid type fuel cells.

28 Although preferred embodiments and their advantages have been described in
29 detail, various changes, substitutions and alterations can be made herein without
30 departing from the spirit and scope of the fuel additives as defined by the appended
31 claims and their equivalents.